

SUPPORTING INFORMATION

Mediated Electrochemistry of Horseradish Peroxidase. Catalysis and Inhibition.

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1. Derivation of equation (3)

At steady state the following equations relate the concentrations of the various forms of the enzyme. They are obtained by expressing the steady state conditions for each form of the enzyme.

$$\text{ES:} \quad k_{1,1}[\text{S}][\text{E}] = (k_{1,-1} + k_{1,2})[\text{ES}], \text{ i.e.,} \quad [\text{E}] = \frac{(k_{1,-1} + k_{1,2})}{k_{1,1}[\text{S}]}[\text{ES}]$$

$$\text{E}_1: \quad k_{1,2}[\text{ES}] + k_{2,-1}[\text{E}_1\text{Q}] = k_{2,1}[\text{Q}][\text{E}_1], \text{ i.e.,} \quad k_{1,2}[\text{ES}] = k_{2,2}[\text{E}_1\text{Q}]$$

$$\text{E}_1\text{Q:} \quad k_{2,1}[\text{Q}][\text{E}_1] = (k_{2,-1} + k_{2,2})[\text{E}_1\text{Q}], \text{ i.e.,} \quad [\text{E}_1] = \frac{(k_{2,-1} + k_{2,2})}{k_{2,1}[\text{Q}]}[\text{E}_1\text{Q}]$$

$$\text{E}_2: \quad k_{2,2}[\text{E}_1\text{Q}] + k_{3,-1}[\text{E}_2\text{Q}] = k_{3,1}[\text{Q}][\text{E}_2], \text{ i.e.,} \quad k_{2,2}[\text{E}_1\text{Q}] = k_{3,2}[\text{E}_2\text{Q}]$$

$$\text{E}_2\text{Q:} \quad k_{3,1}[\text{Q}][\text{E}_2] = (k_{3,-1} + k_{3,2})[\text{E}_2\text{Q}], \text{ i.e.,} \quad [\text{E}_2] = \frac{(k_{3,-1} + k_{3,2})}{k_{3,1}[\text{Q}]}[\text{E}_2\text{Q}]$$

Combining these equations with equation (2) leads to:

$$v_0 = -\left(\frac{d[\text{Q}]}{dt}\right)_{t=0} = k_{2,2}[\text{E}_1\text{Q}] + k_{3,2}[\text{E}_2\text{Q}] = 2k_{2,2}[\text{E}_1\text{Q}] = 2k_{3,2}[\text{E}_2\text{Q}]$$

The above steady state equations may be recast as follows so as to express all enzyme concentrations as a function of one of them, e.g., $[\text{E}_2\text{Q}]$.

$$[\text{E}] = \frac{(k_{1,-1} + k_{1,2})}{k_{1,1}[\text{S}]} \frac{k_{3,2}}{k_{1,2}} [\text{E}_2\text{Q}], \quad [\text{ES}] = \frac{k_{3,2}}{k_{1,2}} [\text{E}_2\text{Q}],$$

$$[\text{E}_1] = \frac{(k_{2,-1} + k_{2,2})}{k_{2,1}[\text{Q}]} \frac{k_{3,2}}{k_{2,2}} [\text{E}_2\text{Q}], \quad [\text{E}_1\text{Q}] = \frac{k_{3,2}}{k_{2,2}} [\text{E}_2\text{Q}],$$

thus leading to the following expression of the initial rate:

$$\frac{2C_E^0}{\nu_0} = \frac{1}{k_{3,2}} \left(1 + \frac{k_{3,-1} + k_{3,2}}{k_{3,1}[Q]_{t=0}} \right) + \frac{1}{k_{2,2}} \left(1 + \frac{k_{2,-1} + k_{2,2}}{k_{2,1}[Q]_{t=0}} \right) + \frac{1}{k_{1,2}} \left(1 + \frac{k_{1,-1} + k_{1,2}}{k_{1,1}C_S^0} \right)$$

or, equivalently,

$$\frac{2C_E^0}{\nu_0} = \frac{1}{k_{3,2}} \left(1 + \frac{K_{3,M}}{[Q]_{t=0}} \right) + \frac{1}{k_{2,2}} \left(1 + \frac{K_{2,M}}{[Q]_{t=0}} \right) + \frac{1}{k_{1,2}} \left(1 + \frac{K_{1,M}}{C_S^0} \right)$$

or

$$\frac{2C_E^0}{\nu_0} = \frac{1}{k_{3,2}} + \frac{1}{k_{3,1}[Q]_{t=0}} + \frac{1}{k_{2,2}} + \frac{1}{k_{2,1}[Q]_{t=0}} + \frac{1}{k_{1,2}} + \frac{1}{k_{1,1}C_S^0}$$

2. Derivation of equation (6)

Equation (5) and the attending initial and boundary conditions may be made dimensionless by way of the following changes of variables and parameters.

$$\tau = \frac{F\nu}{RT} t, \quad y = x \sqrt{\frac{F\nu}{RTD_P}}, \quad q = \frac{[Q]}{C_P^0}, \quad \lambda = \frac{RT}{F} \frac{2k_3 C_E^0}{\nu}, \quad \sigma = k_3 C_P^0 \left(\frac{1}{k_{3,2}} + \frac{1}{k_{1,2}} + \frac{1}{k_{1,1} C_S^0} \right).$$

Thus:

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \frac{\lambda q}{1 + \sigma q}$$

with: $\tau = 0, y \geq 0$ and $y = \infty, \tau \geq 0$: $q = 0, y = 0, t \geq 0$: $q = 1$.

The dimensionless current is given by: $(\partial q / \partial y)_{y=0} = i / FSC_P^0 \sqrt{D_P} \sqrt{F\nu / RT}$.

S-shaped curves as the one shown in figure 5b are typical of a ‘pure catalytic’ situation²¹ corresponding to large values of the kinetic parameter λ , (i.e. high values of k_3 and/or slow scans). The Q profile is then confined within a reaction layer whose thickness is small as compared to the diffusion layer. A steady state is thus established resulting from the mutual compensation of diffusion and chemical reaction, implying that $\partial q / \partial t = 0$ in the above partial derivative equation, which may thus be recast as:

$$\frac{\partial^2 q}{\partial x^2} = \frac{\lambda q}{1 + \sigma q}$$

Integration, taking into account that for $y = \infty, q = 0$ and $\partial q / \partial y = 0$, leads to:

$$-\left(\frac{\partial q}{\partial y} \right)_{y=0} = \sqrt{\frac{2\lambda}{\sigma} \left[1 - \frac{\ln(1 + \sigma)}{\sigma} \right]}$$

and thus to equation (6).

3. Derivation of equation (11)

The steady state condition on each of the various forms of the enzyme now writes:

$$\text{ES:} \quad k_{1,1}[S][E] = (k_{1,-1} + k_{1,2})[ES], \text{ i.e.,} \quad [E] = \frac{(k_{1,-1} + k_{1,2})}{k_{1,1}[S]}[ES]$$

$$\text{E}_1: k_{1,2}[ES] + k_{2,-1}[E_1Q] + k_5[Q][E_3] = k_{2,1}[Q][E_1], \text{ i.e., } k_{1,2}[ES] + k_5[Q][E_3] = k_{2,2}[E_1Q]$$

$$\text{E}_1Q: \quad k_{2,1}[Q][E_1] = (k_{2,-1} + k_{2,2})[E_1Q], \text{ i.e.,} \quad [E_1] = \frac{(k_{2,-1} + k_{2,2})}{k_{2,1}[Q]}[E_1Q]$$

$$\text{E}_2: k_{2,2}[E_1Q] + k_{3,-1}[E_2Q] = k_{3,1}[Q][E_2] + k_4[S][E_2], \text{ i.e., } k_{2,2}[E_1Q] = k_{3,2}[E_2Q] + k_4[S][E_2]$$

$$\text{E}_2Q: \quad k_{3,1}[Q][E_2] = (k_{3,-1} + k_{3,2})[E_2Q], \text{ i.e.,} \quad [E_2] = \frac{(k_{3,-1} + k_{3,2})}{k_{3,1}[Q]}[E_2Q]$$

$$\text{E}_3: \quad k_4[S][E_2] = \{k_5[Q] + k_6\}[E_3]$$

It follows that equation (10) may be rewritten as

$$\frac{\partial[Q]}{\partial t} = D_P \frac{\partial^2[Q]}{\partial x^2} - \left\{ 2 \frac{k_{3,1}k_{3,2}}{k_{3,-1} + k_{3,2}} [Q][E_2] + k_5[Q][E_3] + k_4[S][E_2] \right\}$$

thus leading to equation (11).

4. Derivation of equation (13)

The same dimensionless variables and parameters as in section 2 are used here together with new ones, namely, the concentration of the various forms of the enzymes:

$$e = \frac{[E]}{C_E^0}, \quad e_1 = \frac{[E_1]}{C_E^0}, \quad e_2 = \frac{[E_2]}{C_E^0}, \quad e_3 = \frac{[E_3]}{C_E^0}$$

and three additional kinetic parameters:

$$\chi = \frac{k_{3,-1} + k_{3,2}}{k_{3,1}C_P^0} = \frac{K_{3,M}}{C_P^0}, \quad \rho = \frac{k_4C_S^0}{k_5C_P^0}, \quad \varepsilon = \frac{k_6}{k_5C_P^0}$$

Equation (12) may thus be recast in dimensionless form as:

$$\frac{\partial q}{\partial \tau} = \frac{\partial^2 q}{\partial y^2} - \lambda q e_2$$

Because reaction E_2/E is the rate-determining step of the primary catalytic loop, $[E]$, $[ES]$, $[E_1]$, $[E_1Q]$ are negligible. The three forms remaining into play are E_2 , E_2Q and E_3 . Their concentrations are related by the following steady state equations.

$$[E_2Q] = \frac{k_{3,1}C_P^0}{k_{3,-1} + k_{3,2}}[E_2] = \frac{C_P^0}{K_{3,M}}[E_2], \text{ i.e., } e_2q = \frac{q}{\chi}e_2$$

$$[E_3] = \frac{k_4 C_S^0}{(k_5 [Q] + k_6)} [E_2], \text{ i.e., } e_3 = \frac{\rho}{q + \varepsilon} e_2$$

It follows that:

$$e_2 = \frac{1}{1 + \frac{q}{\chi} + \frac{\rho}{q + \varepsilon}} \text{ and thus:}$$

$$\begin{aligned} \frac{\partial q}{\partial \tau} &= \frac{\partial^2 q}{\partial y^2} - \lambda \frac{q}{1 + \frac{q}{\chi} + \frac{\rho}{q + \varepsilon}} = \frac{\partial^2 q}{\partial y^2} - \lambda \frac{\chi q (q + \varepsilon)}{q(q + \varepsilon) + \chi(q + \varepsilon) + \chi \rho} = \frac{\partial^2 q}{\partial y^2} - \lambda \frac{\chi q^2 + \varepsilon \chi q}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)} \\ &= \frac{\partial^2 q}{\partial y^2} - \lambda \frac{\chi q^2}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)} + \frac{\varepsilon \chi q}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)} \end{aligned}$$

Taking now into account the fact that a ‘pure kinetic’ situation is achieved, the above equation becomes:

$$\frac{\partial^2 q}{\partial y^2} = \lambda \frac{\chi q^2}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)} + \frac{\varepsilon \chi q}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)}$$

Changing y into $y^* = y\sqrt{\lambda}$, and introducing:

$$\varphi = \left(\frac{\partial q}{\partial y^*} \right)_{y^*=0} = \frac{i}{FSC_P^0 \sqrt{D_P} \sqrt{\frac{Fv}{RT}} \sqrt{\lambda}} = \frac{i}{FSC_P^0 \sqrt{D_P} \sqrt{2k_3 C_E^0}}$$

integration of the previous partial derivative equation, according to the same procedure, as in section 2, leads to:

$$\varphi = \sqrt{2} \sqrt{\int_0^1 \frac{\chi q^2 dq}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)} + \int_0^1 \frac{\varepsilon \chi q dq}{q^2 + (\chi + \varepsilon)q + \chi(\rho + \varepsilon)}} = \sqrt{2} \sqrt{I_1 + I_2}$$

$\varphi = 1$ corresponds to the maximal plateau current that can be obtained when E_2/E is the rate-determining step of the primary catalytic loop:

$$i_{pl} = FSC_P^0 \sqrt{D_P} \sqrt{2k_3 C_E^0}$$

i.e., the plateau current in the absence of inhibition and of Michaelis-Menten saturation. φ thus expresses a normalization of the current versus this maximal value.

We now proceed to the integration of the above expression of φ , introducing the function $\text{lms}(\chi, \rho, \varepsilon)$ defined as follows.

$$\text{If } \Delta = (\chi + \varepsilon)^2 - 4\chi(\rho + \varepsilon) < 0:$$

$$I_1 = \chi \left\{ 1 - \frac{\chi + \varepsilon}{2} \ln \left(\frac{1 + \chi + \varepsilon + \chi(\rho + \varepsilon)}{\chi(\rho + \varepsilon)} \right) + \frac{(\chi + \varepsilon)^2 - 2\chi(\rho + \varepsilon)}{\sqrt{-\Delta}} \left[\tan^{-1} \left(\frac{2 + \chi + \varepsilon}{\sqrt{-\Delta}} \right) - \tan^{-1} \left(\frac{\chi + \varepsilon}{\sqrt{-\Delta}} \right) \right] \right\}$$

$$I_2 = \varepsilon\chi \left\{ \frac{1}{2} \ln \left(\frac{1 + \chi + \varepsilon + \chi(\rho + \varepsilon)}{\chi(\rho + \varepsilon)} \right) - \frac{\chi + \varepsilon}{\sqrt{-\Delta}} \left[\tan^{-1} \left(\frac{2 + \chi + \varepsilon}{\sqrt{-\Delta}} \right) - \tan^{-1} \left(\frac{\chi + \varepsilon}{\sqrt{-\Delta}} \right) \right] \right\}$$

If $\Delta = (\chi + \varepsilon)^2 - 4\chi(\rho + \varepsilon) > 0$:

$$I_1 = \chi \left\{ 1 - \frac{\chi + \varepsilon}{2} \ln \left(\frac{1 + \chi + \varepsilon + \chi(\rho + \varepsilon)}{\chi(\rho + \varepsilon)} \right) + \frac{(\chi + \varepsilon)^2 - 2\chi(\rho + \varepsilon)}{2\sqrt{\Delta}} \ln \left(\frac{2 + \chi + \varepsilon - \sqrt{\Delta}}{2 + \chi + \varepsilon + \sqrt{\Delta}} \frac{\chi + \varepsilon + \sqrt{\Delta}}{\chi + \varepsilon - \sqrt{\Delta}} \right) \right\}$$

$$I_2 = \varepsilon\chi \left\{ \frac{1}{2} \ln \left(\frac{1 + \chi + \varepsilon + \chi(\rho + \varepsilon)}{\chi(\rho + \varepsilon)} \right) - \frac{\chi + \varepsilon}{2\sqrt{\Delta}} \ln \left(\frac{2 + \chi + \varepsilon - \sqrt{\Delta}}{2 + \chi + \varepsilon + \sqrt{\Delta}} \frac{\chi + \varepsilon + \sqrt{\Delta}}{\chi + \varepsilon - \sqrt{\Delta}} \right) \right\}$$

If $\Delta = (\chi + \varepsilon)^2 - 4\chi(\rho + \varepsilon) = 0$:

$$I_1 = \chi \left\{ 1 - (\chi + \varepsilon) \ln \left(\frac{1 + \frac{\chi + \varepsilon}{2}}{\frac{\chi + \varepsilon}{2}} \right) - \frac{(\chi + \varepsilon)^2}{4} \left(\frac{1}{1 + \frac{\chi + \varepsilon}{2}} - \frac{1}{\frac{\chi + \varepsilon}{2}} \right) \right\}$$

$$I_2 = \varepsilon\chi \left\{ \ln \left(\frac{1 + \frac{\chi + \varepsilon}{2}}{\frac{\chi + \varepsilon}{2}} \right) + \frac{\chi + \varepsilon}{2} \left(\frac{1}{1 + \frac{\chi + \varepsilon}{2}} - \frac{1}{\frac{\chi + \varepsilon}{2}} \right) \right\}$$

Thus:

$$\text{lms}(\chi, \rho, \varepsilon) = \sqrt{2} \sqrt{I_1 + I_2},$$

leading to equation (13)

5. Derivation of equation (15)

Reactions E/E₁ and E₂/E now jointly govern the kinetics the primary catalytic loop. [E₁], [E₁Q] are still negligible. The forms remaining into play are thus E, ES, E₂, E₂Q and E₃. The following expression of the E₂ concentration follows from the steady state equations of section 3, taking into account that, for the reasons already discussed in the paper, $k_3[\text{Q}] \gg k_4[\text{S}]$.

$$\begin{aligned} e_2 &= \frac{1}{1 + \frac{k_{3,1}C_P^0 q}{k_{3,-1} + k_{3,2}} \left\{ 1 + \frac{k_{3,2}}{k_{1,2}} \left\{ 1 + \frac{(k_{1,-1} + k_{1,2})}{k_{1,1}C_S^0} \right\} \right\} + \frac{k_4 C_S^0}{k_5 C_P^0 q + k_6}} \\ &= \frac{1}{1 + q \left[\frac{k_{3,1}C_P^0}{k_{3,-1} + k_{3,2}} + k_3 C_P^0 \left\{ \frac{1}{k_{1,2}} + \frac{(k_{1,-1} + k_{1,2})}{k_{1,2}k_{1,1}C_S^0} \right\} \right] + \frac{k_4 C_S^0}{k_5 C_P^0 q + k_6}} \end{aligned}$$

$$= \frac{1}{1 + q \left\{ \frac{k_{3,1}C_P^0}{k_{3,-1} + k_{3,2}} + k_3C_P^0 \left(\frac{1}{k_{1,2}} + \frac{1}{k_1C_S^0} \right) \right\} + \frac{k_4C_S^0}{k_5C_P^0q + k_6}}$$

Thus:

$$e_2 = \frac{1}{1 + \frac{q}{\chi'} + \frac{\rho}{q + \varepsilon}} \text{ with } \frac{1}{\chi'} = \frac{1}{\chi} + k_3C_P^0 \left(\frac{1}{k_{1,2}} + \frac{1}{k_1C_S^0} \right)$$

(we may note, by reference to section 2, that $\chi' = 1/\sigma$)

The plateau current is thus given by equation (13) keeping the same values for ρ and ε and replacing χ by χ' .

6. Derivation of equation (16)

At low concentrations of H_2O_2 , and when the 'pure kinetic' conditions are fulfilled, the diffusion-reaction equations pertaining to Q and S write:

$$0 = \frac{\partial[Q]}{\partial t} = D_P \frac{\partial^2[Q]}{\partial x^2} - 2C_E^0 \frac{k_1[S]k_3[Q]}{k_1[S] + k_3[Q]}$$

$$\frac{\partial[S]}{\partial t} = D_S \frac{\partial^2[S]}{\partial x^2} - C_E^0 \frac{k_1[S]k_3[Q]}{k_1[S] + k_3[Q]}$$

Subtracting the first of these equations to the second leads:

$$\frac{\partial \left(2[S] - \frac{D_P}{D_S}[Q] \right)}{\partial t} = D_S \frac{\partial^2 \left(2[S] - \frac{D_P}{D_S}[Q] \right)}{\partial x^2}$$

with as initial and boundary conditions,

$$t = 0, x \geq 0 \text{ and } x = \infty, t \geq 0: [Q] = 0, [S] = C_S^0,$$

$$x = 0, t \geq 0: [Q] = C_P^0 / \left\{ 1 + \exp \left[(F / RT)(E - E_{PQ}^0) \right] \right\}, (\partial[S] / \partial x) = 0$$

The current is given by: $i = FSD_P (\partial[Q] / \partial x)_{x=0}$.

In dimensionless terms, after introduction of $s = [S] / C_P^0$ and of the excess factor

$$\gamma = C_S^0 / C_P^0,$$

$$\frac{\partial \left(2s - \frac{D_P}{D_S}q \right)}{\partial \tau} = \frac{D_S}{D_P} \frac{\partial^2 \left(2s - \frac{D_P}{D_S}q \right)}{\partial y^2}$$

Integration leads to:

$$s_{y=0} = \gamma \left(1 + \frac{1}{2} \frac{D_P C_P^0}{D_S C_S^0} q_{y=0} - I\psi' \right)$$

$$\text{with: } \psi' = \sqrt{\frac{D_P}{D_S}} \frac{C_P^0}{C_S^0} \frac{\psi}{2} = \frac{i}{2FS\sqrt{D_S}C_S^0\sqrt{\frac{Fv}{RT}}} \text{ and } I\psi' = \frac{1}{\sqrt{\pi}} \int_0^\tau \frac{\psi' d\eta}{\sqrt{\tau-\eta}} = \frac{1}{\sqrt{\pi}} \int_{-\infty}^\xi \frac{\psi' d\eta}{\sqrt{\xi-\eta}}$$

Since, as seen next, $q_{y=0}$ is small as compared to 1 because the wave occurs at a more positive potential than the standard potential of the P/Q couple. It follows that:

$$s_{y=0} \approx \gamma(1 - I\psi')$$

The dimensionless expression of the catalytic current may be recast from section 2 as:

$$\frac{\sigma^2 \psi^2}{2\lambda(s_{y=0})^2} = \sigma \frac{q_{y=0}}{s_{y=0}} - \ln \left(1 + \sigma \frac{q_{y=0}}{s_{y=0}} \right),$$

taking into account the fact that, because the substrate concentration is small the expression of the parameter σ simplifies to:

$$\sigma = \frac{k_3 C_P^0}{k_1 C_S^0}$$

Kinetic control by reaction (1) and by the diffusion of the substrate requires large values of σ . It follows that in the above expression of the current, the log term may be neglected leading to:

$$\frac{\sigma \psi^2}{2\lambda q_{y=0}} = s_{y=0} = \gamma[1 - I\psi']$$

and therefore:

$$\frac{\psi'^2 [1 + \exp(-\xi)]}{\frac{\lambda}{2\gamma\sigma} \frac{D_P}{D_S}} = [1 - I\psi']$$

Introducing a new potential variable:

$$\xi' = \xi + \ln \left(\frac{D_P}{D_S} \frac{RT}{F} \frac{k_1 C_E^0}{v} \right) = -\frac{F}{RT} (E - E') \text{ with:}$$

$$E' = E_{PQ}^0 + \frac{RT}{F} \ln \left(\frac{D_P}{D_S} \frac{RT}{F} \frac{k_1 C_E^0}{v} \right)$$

It follows, since the kinetic term is large, that the equation of the wave becomes:

$$\psi'^2 \exp(-\xi') = 1 - I\psi'$$

leading to a wave that is under complete control of the substrate diffusion and is shifted toward positive potentials as compared to the standard potential of the P/Q couple. The peak characteristics are:^{20c}

$$\psi'_p = 0.609, \xi'_p = 0.409, \xi'_p - \xi'_{p/2} = 1.41.$$

Thus:

$$i_p = 2 \times 0.609 FS \sqrt{D_S} C_S^0 \sqrt{\frac{Fv}{RT}}$$

7. Derivation of equations (18) and (19)

Equations (17) may be recast as follows, after introduction of the dimensionless form of the enzyme concentrations, e_2 , e_2q , and e_3 .

$$\frac{\partial e_2}{\partial t} = -\left(k_{3,1}C_P^0q + k_4C_S^0\right)e_2 + (k_{3,-1} + k_{3,2})e_2q + \left(k_5C_P^0q + k_6\right)e_3$$

$$\frac{\partial e_2q}{\partial t} = k_{3,1}C_P^0qe_2 - (k_{3,-1} + k_{3,2})e_2q$$

$$\frac{\partial e_3}{\partial t} = k_4C_S^0e_2 - \left(k_5C_P^0q + k_6\right)e_3$$

with, at $t = 0$, $e_2 = e_2^0 = k_6 / (k_4C_S^0 + k_6)$, $e_2q = 0$, $e_3 = e_3^0 = k_4C_S^0 / (k_4C_S^0 + k_6)$.

Laplace transformation of this set of differential equations (the Laplace variable is noted s), taking the initial conditions into account, leads to:

$$\left(s + k_{3,1}C_P^0q + k_4C_S^0\right)\bar{e}_2 - (k_{3,-1} + k_{3,2})\bar{e}_2q - \left(k_5C_P^0q + k_6\right)\bar{e}_3 = e_2^0$$

$$-k_{3,1}C_P^0q\bar{e}_2 + \left(s + k_{3,-1} + k_{3,2}\right)\bar{e}_2q = 0$$

$$-k_4C_S^0\bar{e}_2 + \left(s + k_5C_P^0q + k_6\right)\bar{e}_3 = e_3^0$$

The second of these equations may be simplified into:

$$-k_{3,1}C_P^0q\bar{e}_2 + (k_{3,-1} + k_{3,2})\bar{e}_2q = 0 \text{ (equivalent to } \partial e_2q / \partial t = 0 \text{ in original space)}$$

since the rate constants in the primary catalytic cycle are fast. Therefore:

$$\bar{e}_2 = \frac{e_2^0}{\left(1 + \frac{q_{x=0}}{\chi}\right) \left\{s + \frac{k_4C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5C_P^0q_{x=0} + k_6\right\}} + \frac{k_5C_P^0q_{x=0} + k_6}{\left(1 + \frac{q_{x=0}}{\chi}\right) \left\{s + \frac{k_4C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5C_P^0q_{x=0} + k_6\right\}}$$

$$e_2 = \frac{e_2^0}{1 + \frac{q_{x=0}}{\chi}} \exp\left[-\left(\frac{1}{1 + \frac{q_{x=0}}{\chi}} + \frac{q_{x=0} + \varepsilon}{\rho}\right)k_4C_S^0t\right] + \frac{1}{1 + \frac{q_{x=0}}{\chi} + \frac{\rho}{q_{x=0} + \varepsilon}} \left[1 - \exp\left[-\left(\frac{1}{1 + \frac{q_{x=0}}{\chi}} + \frac{q_{x=0} + \varepsilon}{\rho}\right)k_4C_S^0t\right]\right]$$

or:

$$e_2 = \frac{e_2^0}{1 + \frac{q_{x=0}}{\chi}} \exp \left\{ - \left(\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right) t \right\}$$

$$+ \frac{1}{\left(1 + \frac{q_{x=0}}{\chi} + \frac{k_4 C_S^0}{k_5 C_P^0 q_{x=0} + k_6} \right)} \left[1 - \exp \left\{ - \left(\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right) t \right\} \right]$$

leading finally to equation (18).

\bar{e}_3 may likewise be obtained from the above set of linear equations leading to:

$$\bar{e}_3 = \frac{e_3^0}{s + k_5 C_P^0 q_{x=0} + k_6} + \frac{e_2^0 k_4 C_S^0}{\left(1 + \frac{q_{x=0}}{\chi} \right) (s + k_5 C_P^0 q_{x=0} + k_6) \left\{ s + \frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right\}}$$

$$+ \frac{k_4 [S] (k_5 C_P^0 q_{x=0} + k_6)}{\left(1 + \frac{q_{x=0}}{\chi} \right) s (s + k_5 C_P^0 q_{x=0} + k_6) \left\{ s + \frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right\}}$$

and therefore to:

$$e_3 = e_3^0 \exp \left\{ - (k_5 C_P^0 q_{x=0} + k_6) t \right\} + e_2^0 \left[\exp \left\{ - (k_5 C_P^0 q_{x=0} + k_6) t \right\} - \exp \left\{ - \left(\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right) t \right\} \right]$$

$$+ \frac{\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} - \left(\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right) \exp \left\{ - (k_5 C_P^0 q_{x=0} + k_6) t \right\} + (k_5 C_P^0 q_{x=0} + k_6) \exp \left\{ - \left(\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right) t \right\}}{\left(\frac{k_4 C_S^0}{1 + \frac{q_{x=0}}{\chi}} + k_5 C_P^0 q_{x=0} + k_6 \right)}$$

i.e., to equation (19).